

REMARKS

Claim 10 has been rejected under 35 USC §112, second paragraph as containing both a broad range or limitation and a narrow range or limitation falling within that broader range or limitation. Applicants have amended this claim and have created dependent claims 18 and 19 to recite the narrow range or limitation. Claim 16 has been rejected under 35 USC §§101 and 112, second paragraph, as being an improper process claim, and also for indefiniteness. This claim has also been amended.

Claim 7 has been rejected under §112 for use of the phrase "formulation auxiliaries." This phrase is found at page 5, line 25, of the present specification, and examples of such formulation auxiliaries are given in detail on the ensuing pages. For example, on page 6, lines 8-15, binders are discussed, and on the same page, lines 17-26, protective agents are discussed. Applicants respectfully submit that one of ordinary skill in the art would understand the claimed scope encompassed by the phrase "formulation auxiliaries" from these and other cites in the specification.

Claim 16 has also been rejected under §112, second paragraph for use of the phrase "or of the preservative for acid treatment." The word "preservative" refers to a formulation utilizing impregnated salts, as in claim 6, and "for acid treatment" refers to use of the impregnated salt, or the preservative made from this salt, in an acid treatment process. Claim 21 has been created to make the intended meaning more clear. Applicants respectfully request reconsideration of the rejections of claims 7, 10 and 16 under 35 USC §101 and §112, second paragraph.

The abstract included with the replacement specification begins on a new page

BROECKEL et al. Serial No. 09/487,000

as required by 37 CFR 1.52(b)(1). The replacement specification is double spaced.

The trademarks Sipernat, Tixosit and Aerosil have been identified in each instance they are used in the specification, and generic terminology giving the nature of these products has been included in these places.

Claims 1-16 have been rejected under 35 USC 103(a) as unpatentable over van Ooijen (EP 0 608 975 A1) or Gonthier et al. (US 3,600,198) or Kotani et al. (US 4,122,187). These rejections are respectfully traversed. Applicants submit that one of ordinary skill in the art would not find the presently claimed invention obvious in light of the above references.

Van Ooijen discloses compositions of an alkali or alkaline earth metal hydroxycarboxylate salt, which is a liquid or semi-solid at ambient temperatures, combined with an aliphatic carboxylic acid having a pKa value lower than the hydroxycarboxylic acid form of the hydroxycarboxylate salt (abstract and page 2, lines 20-22). Van Ooijen additionally states that hydroxycarboxylic acids such as lactic acid and gluconic acid "are the most suited to this technique due to their syrupy and hygroscopic nature" (page 2, line 36), and gives "[s]pecific examples of the preferred aliphatic carboxylic acids[, namely] *trans*-fumaric acid [], maleic acid [], malonic acid [], and methyl-malonic acid" (page 2, lines 52-54). Van Ooijen also states that the hydroxycarboxylate salt and the aliphatic carboxylic acid may be combined either in the form of two solids or as a liquid impregnated in a solid (page 3, lines 11-14). The amount of aliphatic carboxylic acid to be included ranges from 1 to 90% by weight, with 40-60% aliphatic carboxylic acid being preferred, and equimolar amounts of

BROECKEL et al. Serial No. 09/487,000

hydroxycarboxylate salt and aliphatic carboxylic acid being "most preferred" (page 3, lines 19-21).

The presently claimed invention differs from this disclosure in that the carboxylate salts are not limited to hydroxycarboxylate salts, the carboxylic acids utilized are not required to have pKa values lower than the functionalized carboxylates, the amount of carboxylic acid required is in a range lower than the preferred amounts and this range extends below that disclosed by van Ooijen. Applicants respectfully assert that these differences, taken together, would not be obvious from the disclosure given in van Ooijen. This is primarily so due to the disclosure requiring and teaching limitations not found in the present invention.

To establish *prima facie* obviousness, some suggestion or motivation to modify the reference must be found either in the reference itself or in the knowledge generally available to one of ordinary skill in the art (*In re Fine*, 837 F.2d 1071, 5 USPQ2d 1596 (Fed. Cir. 1988)). Additionally, the prior art must be considered in its entirety, including portions that would lead away from the claimed invention (*W. L. Gore & Associates, Inc., v. Garlock, Inc.*, 721 F.2d 1540, 220 USPQ 303 (Fed. Cir. 1983)). As discussed above, van Ooijen *requires* that the aliphatic carboxylic acid have a pKa value lower than that of the functionalized hydroxycarboxylic acid. The difference in pKa values is disclosed by van Ooijen to be the factor that enables the hydroxycarboxylic acid to be released as both substances first ionize and then the carboxylate salt forms preferentially. This requirement teaches away from the present invention as claimed, where the carboxylate salt and the carboxylic acid need not have pKa values as

BROECKEL et al. Serial No. 09/487,000

required by van Ooijen. Accordingly, the disclosure of van Ooijen would not suggest or give motivation to make the present invention, as pKa values are taught to be critical to the function of the invention.

Furthermore, the composition disclosed by van Ooijen would be rendered unsatisfactory for its intended purpose, were it to be modified in a manner consistent with the presently claimed invention, as the mechanism of action is disclosed therein to be dependent on the relative pKa values (page 2, lines 26-32). According to van Ooijen, only compounds having carboxylic acids with pKa values lower than those of the functionalized hydroxycarboxylates are satisfactory. Other combinations do not enable the reaction to progress, according to the mechanism of action, and therefore would not be of value. Such other combinations would change the principle of operation as it has been given in van Ooijen. One of ordinary skill in the art would not be motivated, therefore, by van Ooijen to modify that reference to encompass more than the disclosed hydroxycarboxylate salts and carboxylic acids (*In re Gordon*, 733 F.2d 900, 221 USPQ 1125 (Fed. Cir. 1984), *In re Ratti*, 270 F.2d 810, 123 USPQ 349 (CCPA 1959)).

Van Ooijen also teaches away from the present invention as claimed in the amount of carboxylic acid to be used in the compound. In the present invention, significantly less carboxylic acid is needed to accomplish the purposes of the invention. Van Ooijen discloses generally that the carboxylic acid may be present in amounts as low as 1% by weight, but states that preferably, the carboxylic acid should be at least 40% by weight, and that equimolar amounts (50% by weight) are optimal. These

values teach away from the claimed range of the present invention, 0.5% to 30% carboxylic acid by weight, and are understandably preferred, given the disclosed mechanism of action. To ensure full formation of the hydroxycarboxylic acid, an equal amount of carboxylate should be formed to absorb the metal ions given off. Less than 50% by weight of carboxylic acid would give a result that would not optimize the invention as disclosed in van Ooijen, and an amount of 0.5% to 30% by weight would likely be avoided. Such an amount of carboxylic acid would not absorb a sufficient number of metal ions to ensure full release of the hydroxycarboxylic acid.

The objective of the present invention, to provide organic acids in a form suitable for acidifying and preserving human and animal food, maximizing the active substance content while minimizing undesired odors, and providing these in suitable solid form with good storage, flow and processing properties (specification, page 1, lines 18-23 and page 2, lines 13-20) is significantly different from the object of van Ooijen. In that reference, a desire for storage of the hydroxycarboxylic acid and its complete release at a precise point in time led to the compound therein. These different objectives have led to significantly different inventions.

Using the carboxylate salt with only a small amount of carboxylic acid, rather than an equimolar amount, gives a compound with a high active substance content (e.g., 68 to 75% by weight; page 3, lines 12-17 of the specification). The amount of carboxylic acid utilized, however, is sufficient to reduce the undesired, highly pungent, odor (page 3, lines 11-12 of specification). Furthermore, the compounds of the presently claimed invention allow the active carboxylic acid to be released efficiently

BROECKEL et al. Serial No. 09/487,000

and rapidly when applied in their intended use. This use is different from that in van Ooijen, where the active hydroxycarboxylic acid is fully released at one time in a solution. The smaller amount of carboxylic acid utilized in the presently claimed invention also ensures good flow properties without the need for release agents, though these may still be added to enhance flow rates (page 4, lines 22-27 and 32-35), and gives improved storage properties overall (see table 1, pages 12-13 of specification).

The present invention as claimed proceeds in a direction which is significantly different from that set forth in van Ooijen, as shown in the above analysis. Proceeding in a direction different from others in the art produces unexpected results, which in turn provide objective evidence of nonobviousness (*Specialty Composites v. Cabot Corp.*, 6 USPQ 2d 1601 (Fed. Cir. 1988)). The improved storage properties given by limitation of the carboxylic acid content to less than 30% is unexpected, as van Ooijen gives no indication of such an improvement being either possible or desirable. The maximization of hydroxycarboxylic acid formation in a solution, with contemporaneous formation of insoluble carboxylate salts, is the only objective of note in that disclosure, and that objective is optimized by a carboxylic acid content of 50%.

Applicants submit, therefore, that van Ooijen does not suggest or give motivation to create the presently claimed invention, and that unexpected results have been obtained by limitation of carboxylic acid content. Accordingly, applicants respectfully request that the rejection of claims 1-3, 5 and 16 under 35 USC §103(a) over van Ooijen be withdrawn.

Claims 4, 6 and 12 have also been rejected under 35 USC §103(a) over van

BROECKEL et al. Serial No. 09/487,000

Ooijen. As to claim 4, the examiner states that van Ooijen "does not exclude using the same salt which would breakdown [sic] to the same acid" (page 5 of the office action). It is applicants' understanding that the disclosed mechanism of action in van Ooijen *requires* that the aliphatic carboxylic acids utilized therein have a lower pKa than the functionalized hydroxycarboxylate salt. When the hydroxycarboxylic acid is liberated, "the aliphatic carboxylate ion combines preferentially with the alkali(ne earth) metal ions," due to the lower pKa (page 1, lines 30-31, see also lines 26-32, of van Ooijen). For this preferential combination to occur, the competing hydroxycarboxylate and carboxylate ions must have differing pKa values, and accordingly, must be from different acids. Therefore, applicants submit that claim 4 is not obvious under 35 USC §103(a) over van Ooijen, and request that the rejection be withdrawn.

The examiner has rejected claim 6 by stating that the claimed ingredients of van Ooijen are disclosed to possess preservative qualities, and that it would have been obvious, therefore, to use the presently claimed compositions, with their preservative qualities. Applicants have argued above that the compositions of the presently claimed invention are not obvious under 35 USC §103(a) over van Ooijen, and applicants here submit that use of these compounds as preservatives would, therefore, also be unobvious. Applicants accordingly request that the rejection of claim 6 be withdrawn. Applicants further request that the rejection of claim 12 under 35 USC §103(a) be withdrawn, as it depends from claim 1 and therefore incorporates all of the limitations of that claim.

Claims 1-6 have been rejected under 35 USC §103(a) over Gonthier. This

BROECKEL et al. Serial No. 09/487,000

reference discloses compositions of buffered propionic acid and buffered benzoic acid for use as biocides in the preservation of fish. No mention of impregnation of the propionate or benzoate salts with propionic acid or benzoic acid is made therein, and the mixtures are produced for their synergistic effects. As this reference does not concern or discuss the impregnation of salts, applicants respectfully submit that it is not analogous and should not be used as a prior art reference.

In addition, there is no suggestion or motivation for limiting the amount of propionic or benzoic acid, or impregnating the acid in the salt for any purpose, including for production of compounds with the improved characteristics discussed above. Accordingly, applicants respectfully request the examiner to withdraw the rejection of claims 1-6 under 35 USC §103(a) over Gonthier.

Claims 1-10 and 12 have been rejected under 35 USC §103(a) over Kotani. This reference discloses use of sorbic acid and double salts of sorbic acid with the addition of glycerin to give "improved workability" (col. 1, line 47). The double salts of sorbic acid are produced by dissolution of the sorbic acid in 90% ethanol, with potassium sorbate being added in an equimolar amount and the resulting mixture being allowed to crystallize (Kotani, col. 2, lines 52-64). The examiner characterizes Kotani as disclosing "the claimed salts and acid[s]" of claims 1-7 of the present invention, the use of the protective agents of claims 8-10, and impregnation of claim 12. Applicants respectfully submit that the sorbic acid double salts are not the same as the salts of claims 1-7, nor are these salts obvious from the disclosure of Kotani. Additionally, applicants submit that as claims 8-10 depend from claim 1, they, too are unobvious in light of this



disclosure, and that Kotani does not, in fact, disclose the impregnation process as in claim 12.

The salts of present claim 1, and therefore of all claims, are carboxylate salts that have been impregnated with from 0.5 to 30% by weight "of at least one liquid carboxylic acid" (claim 1). Applicants submit that one of ordinary skill in the art, upon reading the specification, would understand the phrase "liquid carboxylic acid" to denote a "carboxylic acid, which is liquid at 40°C or below" (specification, page 4, line 12). The carboxylic acid of Kotani, sorbic acid, has a melting point of 134.5°C ("sorbic acid" entry of [www.chemfinder.com](http://www.chemfinder.com)), and therefore is not "liquid at 40°C or below." Kotani seeks to "provide powdery sorbic acids having improved workability," which "[do] not scatter in handling and [do] not give out an irritating odor" (col. 1, lines 46-50). These objectives are met by introducing glycerin into either "sorbic acid or a double salt thereof" (i.e., not *solely* the double salt) (abstract, claim 1 of Kotani, emphasis supplied), and no indication is given that a combination of a liquid carboxylic acid and a carboxylate salt would accomplish any of the objectives, or that such a combination would be desirable for any purpose. Applicants therefore respectfully submit that one of ordinary skill in the art would not be motivated by Kotani to create the presently claimed invention, and that no reasonable expectation of success is found in that reference.

Claims 8-10 are to a preservative made from the impregnated salts of claim 1, combined with protective agents. Applicants respectfully submit that the impregnated salts of the present invention are not disclosed or suggested in Kotani, and therefore that the disclosure of certain protective agents would not be sufficient to render these

BROECKEL et al. Serial No. 09/487,000

claims obvious under 35 USC §103(a).

Further, as Kotani utilizes a process for producing the double salts of sorbic acid that is entirely different from the impregnation process of the present invention as claimed, applicants submit that claim 12 is not rendered obvious by the disclosure therein. As stated above, the double salts of sorbic acid are produced by dissolution of sorbic acid in 90% ethanol, to which potassium sorbate is added in an equimolar amount, with the resulting mixture being allowed to crystallize (Kotani, col. 2, lines 52-64). In contrast, the present invention states that "[t]he term impregnation means applying at least one carboxylic acid, which is liquid at 40°C or below, to the solid carboxylic acid salt(s) so that the liquid carboxylic acid(s) penetrate(s) into the salt crystal(s)" (specification, page 4, lines 11-14). According to this definition, the process disclosed by Kotani is not impregnation as one of ordinary skill in the art would understand this term upon reading the specification. Accordingly, applicants submit that claim 12 is not rendered obvious by the disclosure in Kotani. Applicants respectfully request, therefore, that the examiner withdraw the rejections of claims 1-10 and 12 made under 35 USC §103(a) over Kotani.

Applicants also request that the examiner reconsider and withdraw the rejections of claims 11 and 14-15 under 35 USC §103(a), as these are also directly or indirectly dependent from claim 1 and/or for the pertinent reasons given above.

In view of the foregoing amendments and remarks, applicants consider that the rejections of record have been obviated and respectfully solicit passage of the application to issue.

BROECKEL et al. Serial No. 09/487,000

Please charge any shortage in fees due in connection with the filing of this paper, including Extension of Time fees to Deposit Account No. 11-0345. Please credit any excess fees to such deposit account.

Respectfully submitted,

KEIL & WEINKAUF

A handwritten signature in cursive script, appearing to read "Herbert B. Keil".

Herbert B. Keil  
Reg. No. 18,967

1101 Connecticut Ave., N.W.  
Washington, D.C. 20036  
(202)659-0100

HBK/DCL/mks

**VERSION WITH MARKINGS TO SHOW CHANGES MADE IN THE SPECIFICATION**  
**IN THE SPECIFICATION**

Please replace the entire specification with the replacement specification attached hereto.

Impregnated salts, their production and their use

The present invention relates to impregnated salts comprising at least one salt of one or more carboxylic acids, which salt has been impregnated with from 0.5 to 30% by weight, based on the carboxylic acid salt, of at least one carboxylic acid, and to preservatives comprising an impregnated salt and, where appropriate, at least one carrier and/or formulation auxiliaries, it being possible for the preservatives to be coated with a protective agent and/or a dusting powder.

The invention furthermore relates to a process for producing the impregnated salts and the preservatives, and to the use of the salts and preservatives for the treatment of human and animal food, and for use in silage.

Short-chain organic acids such as formic acid, acetic acid or propionic acid are used for acidifying and preserving human and animal food. Disadvantages of these acids are, for example, their liquid state of aggregation at room temperature, the sharp or pungent odor resulting from the low vapor pressure, and their corrosiveness.

BROECKEL et al. Serial No. 09/487,000

In addition, the liquid organic acids can be incorporated in concentrated form, for example into animal food, only with considerable technical complexity.

DE 28 33 727 A1 discloses a particulate fungicidal material which comprises propionic acid and a carrier material. It is said that with this material there is no increase in the number of mold colonies on stored agricultural harvest products even after incubation for several days. However, it has emerged that material of this type is itself not stable on storage (loss of acid), and the maximum amount of propionic acid which can be applied depends greatly on the carrier material used. In addition, unpleasant odors arise with this material owing to evaporation of the propionic acid.

EP-A-0 590 856 and EP-A-0 608 975 disclose mixtures of solid carboxylic acid salts and solid carboxylic acids with a lower pKa than the carboxylic acid in the salts used. When this mixture is dissolved in water, the carboxylic acids are liberated from the salts by the carboxylic acid with the lower pKa in a displacement reaction. The resulting new salts with the carboxylic acid with the lower pKa are advantageously insoluble in water and precipitate from the solution. A disadvantage of these mixtures is that it is still necessary to use various carboxylic acids with different pKa values for producing the preservatives. In order to ensure that the carboxylic acids are completely liberated from the initial carboxylic acid salts (for example from calcium propionate) on dissolving in water, the carboxylic acids with the lower pKa (for example maleic acid) must be added

BROECKEL et al. Serial No. 09/487,000

in at least equimolar amounts based on the carboxyl groups present in the acids. This limits the individual carboxylic acid active substance content. If insoluble carboxylic acid salts are formed in this liberation, they must additionally be removed in a subsequent reaction.

It is an object of the present invention to provide novel compositions for treating human and animal food which do not have the abovementioned disadvantages and can easily be mixed by the user without difficulty into the human and animal food to be treated. The main aim was to produce a solid composition which has a maximum active substance content and displays very little odor, if any. The solid final product should have good storage, flow and processing properties.

We have found that this object is achieved by the novel impregnated salts comprising at least one salt of one or more carboxylic acids, which salt has been impregnated with from 0.5 to 30% by weight, based on the carboxylic acid salt, of at least one liquid carboxylic acid.

The invention additionally relates to preservatives comprising an impregnated salt of the abovementioned composition. In addition, the preservatives may advantageously comprise at least one carrier and/or formulation auxiliary and, where appropriate, be coated with a protective agent and/or dusting powder.

BROECKEL et al. Serial No. 09/487,000

The invention furthermore relates to a process for producing the impregnated salts, which comprises impregnating at least one salt of a carboxylic acid or of a mixture of carboxylic acids with at least one liquid carboxylic acid until the concentration is 30% by weight based on the carboxylic acid salt.

The invention additionally relates to the production of preservatives comprising an impregnated salt of the abovementioned composition, which comprises impregnated salts comprising at least one salt of one or more carboxylic acids, which salt has been impregnated with from 0.5 to 30% by weight of at least one liquid carboxylic acid being mixed where appropriate with at least one carrier and/or at least one formulation auxiliary, and being agglomerated with or without addition of one or more binders, and subsequently the preservatives advantageously being provided with a protective agent which solidifies at room temperature (235C), the protective agent being added in an amount such that the resulting preservatives are coated and, where appropriate, further odorization is effected by, for example, adding fragrances. The preservatives produced in this way may advantageously also be coated with a finely dispersed dusting powder to improve the flow properties of the preservatives.

The novel impregnated salts or preservatives have the advantage that the highly pungent odor of the acid is reduced. The impregnated salts advantageously comprise an active substance content of from 68 to 75% by weight, preferably 70 to 73% by

BROECKEL et al. Serial No. 09/487,000

weight, particularly preferably 70 to 72% by weight, as total based on the total amount of carboxylic acids present in the salt and added. Both the novel impregnated salts and the preservatives release the acid content efficiently and rapidly from the solid and have good storage, flow and processing properties.

Liquid organic acids suitable for impregnating the carboxylic acid salts are acids or mixtures of acids which are liquid or become liquid at the processing temperatures, preferably down to 405C or below.

C<sub>1</sub>-C<sub>8</sub>-mono- and/or dicarboxylic acids and the salts of these C<sub>1</sub>-C<sub>8</sub>-mono- and/or dicarboxylic acids are advantageously used to produce the impregnated salts or to produce the preservatives. Alkali metal, alkaline earth metal or ammonium salts are suitable. Acids such as formic, acetic and/or propionic acid and their ammonium, calcium, lithium, sodium, magnesium and/or potassium salts are preferably used. The calcium, sodium or ammonium salts are advantageously used. However, also suitable in principle are other acids such as amino acids, hydroxy carboxylic acids, oxo acids or mineral acids such as HCl or H<sub>2</sub>SO<sub>4</sub> and their salts, with mineral acids being less preferred. It is possible to use single salts or mixtures of different salts of one carboxylic acid or several carboxylic acids which have been impregnated with one or more acids to produce the impregnated salts. The impregnated salts advantageously consist of the salts of a carboxylic acid which have been impregnated with the same carboxylic acid.



BROECKEL et al. Serial No. 09/487,000

The impregnated salts preferably consist of the salt of a carboxylic acid which has been impregnated with the same carboxylic acid. Salts of formic acid and/or propionic acid which have been impregnated with formic acid and/or propionic acid in a form which is as concentrated as possible, for example with 99% strength formic acid, are particularly preferred. Impregnated salts produced from formic acid and the salts of formic acid are very particularly preferred.

X-Ray structural analysis of the novel impregnated salts shows an additional band by comparison with normal carboxylic acid salts.

The impregnated salts can, to improve handling, advantageously be mixed with other substances, for example with a carrier, and/or be dusted with a dusting powder.

The term impregnation means applying at least one carboxylic acid, which is liquid at 40°C or below, to the solid carboxylic acid salt(s) so that the liquid carboxylic acid(s) penetrate(s) into the salt crystal(s). As a rule, this takes place with slight evolution of heat. For the impregnation, at least one carboxylic acid is applied in an amount of up to 30% by weight, based on the carboxylic acid salt(s), onto the salt(s), preferably applying the carboxylic acid(s) in an amount of from 0.5 to 30% by weight, particularly preferably applying from 15 to 25% by weight, very particularly preferably applying from 15 to 20% by weight, based on the salt component, to produce a solid substance as reaction

BROECKEL et al. Serial No. 09/487,000

product. With more than 30% by weight of acid, the salt crystals start to stick together; under these conditions, free carboxylic acid is present to some extent in addition to the impregnated salts. These crystals which are stuck together can be separated from one another by adding a release agent, and the free carboxylic acid can be taken up by the release agent. With more than 35% by weight of acid, the products stick together so strongly that a pasty texture results as a consequence of the free carboxylic acid. These pasty textures can be processed to granules for example in another working step by addition of a release agent and treatment in, for example, a mixer. Since further working steps and larger amounts of a release agent are necessary if more than 30% by weight of free acid is added, these embodiments are less preferred for economic reasons. However, it is possible in principle to improve the flow properties of the impregnated salts by adding small amounts of a release agent even with less than 30% by weight of carboxylic acid. Examples of suitable and advantageous release agents are Sipernats® (highly disperse silica supplied by Degussa), Aerosils® (silica supplied by Degussa) and/or Tixosils® (silica).

Thus, in the novel process for producing the impregnated salts, at least one salt of a carboxylic acid or of a mixture of carboxylic acids is impregnated with at least one carboxylic acid which is liquid at 405C or below until the concentration is 30% by weight based on the carboxylic acid salt(s).

BROECKEL et al. Serial No. 09/487,000

It is also possible in the novel process for producing the impregnated salts to add at least one salt of one or more carboxylic acids to at least one carboxylic acid. This mode of production is less favorable than addition to the salt(s) so that under these conditions, for example when a mixer is used for production, an increased energy input is necessary.

The novel process for producing impregnated salts is advantageously carried out at a temperature determined by the solidification point of the carboxylic acid used. The process is carried out at from 0 to 605C, preferably from 15 to 505C, particularly preferably from 20 to 405C.

In a preferred embodiment, the novel salt also has a protective agent and/or dusting powder on the surface of the crystals. The size of the impregnated salt crystals is preferably below 2.5 mm, particularly preferably from 10  $\mu\text{m}$  to 2000  $\mu\text{m}$ , very particularly preferably from 300  $\mu\text{m}$  to 1500  $\mu\text{m}$ .

The novel preservatives mean preservatives comprising impregnated salts which comprise at least one salt of one or more carboxylic acids and have been impregnated with at least one liquid carboxylic acid. These impregnated salts can be mixed in the preservatives with one or more carriers and/or formulation auxiliaries. It is possible in the novel process for producing the preservatives to agglomerate this mixture with or

BROECKEL et al. Serial No. 09/487,000

without addition of binder. It is then possible to apply to these preservatives a protective agent which is soluble or swellable in water at 205C and/or a finely dispersed dusting powder so that the novel preservatives have a coating of a protective agent and/or dusting powder.

Carriers which can be employed are porous, organic or inorganic carrier materials whose particle sizes are from 1  $\mu\text{m}$  to 1,000  $\mu\text{m}$ , preferably from 5  $\mu\text{m}$  to 100  $\mu\text{m}$ .

Suitable in principle for producing such free-flowing, reduced odor agglomerates are all known organic or inorganic porous carriers as long as they are resistant to acid.

Examples are cereal brans, perlite, clay materials, silicates and silicas, with inorganic carriers being preferred because their properties can be controlled better.

Examples of other carriers which can be used are diatomaceous earth, crushed sand, clay, nylon powder, insoluble metal oxides or insoluble metal salts, Aerosil<sup>®</sup> (silica supplied by Degussa), corundum, ground glass, granite, quartz or flint, aluminum phosphate, kaolin, bentonite, zeolites, calcium silicate, talc, titanium oxide, active carbon or bonemeal.

Carriers which are preferably used are cereal brans, silicates, perlite or silicas in amounts of from 10% to 70%, preferably 20 to 40%, of the weight of the impregnated

salt.

Suitable binders in the novel process are water and/or synthetic or natural polymers, for example albumin, casein, soybean protein, starch, synthetic cellulose derivatives such as carboxymethylcellulose, methylcellulose, hydroxymethyl-, hydroxyethyl- and/or -propylcellulose, polyethylene glycol, polyvinyl alcohol, polyvinylpyrrolidone, gelatin, carrageenan, chitosan, dextrin, alginates, agar-agar, gum arabic, tragacanth or guar gum, or mixtures thereof.

Protective agents which can be used are water-soluble polymers such as synthetic or natural polymers, for example gelatin, carrageenan, alginates or polyvinyl pyrrolidone, organic acids, their salts or low-melting inorganic salts.

Protective agents which are preferably used are polyethylene glycols, polyvinylpyrrolidones or C<sub>3</sub>-C<sub>14</sub>, preferably C<sub>3</sub>-C<sub>6</sub>, organic acids and their salts, in particular citric acid, fumaric acid, succinic acid, adipic acid, benzoic acid and their salts, or amino acids and their salts.

In a preferred embodiment of the novel process for producing the preservatives, the carboxylic acid salt is introduced into a mixer, impregnated with the organic acid, a carrier is admixed where appropriate, and subsequently agglomeration and coating with

the protective agent are carried out in the presence or absence of a binder.

The impregnated salts and/or carrier particles are mixed with the protective agent, the latter ordinarily consisting of a highly concentrated solution or melt of substances which are soluble or swellable in water and solidify at room temperature (235C). This protective agent is preferably applied in the heated state to the impregnated salt and/or carrier particles and mixed with the latter. During this, the protective agent solidifies on the surface of the impregnated salts and/or carrier particles. Suitable mixer operating parameters result in agglomeration of different particles to larger granules.

The size of the granules can be adjusted by processing parameters, for example during the mixing or during the fluidized bed granulation, and by the amount and type of binder or else by subsequent screening or grinding. The granules preferably have an average diameter of less than 3 mm, in particular of 0.3 - 1.3 mm. It is possible where appropriate for residual water to be present in the protective agent used for coating and agglomeration. After the agglomeration process or directly after production of the impregnated salts, residual water can be bound by a dusting process with a dry and finely dispersed dusting powder. It is possible by this dusting process also to prevent the agglomerates or impregnated salts sticking together later and, in addition, to apply, for example, the salt of the organic acid used (eg. sodium or calcium formate or propionate) to the agglomerate or the salts. It is furthermore possible where appropriate

BROECKEL et al. Serial No. 09/487,000

to add a fragrance or flavoring, eg. vanillin, tecu flavor, citral or fructin, which makes it possible to achieve an additional odor-masking effect which, for example, makes the food attractive for animals to consume.

Protective agents which are preferably employed, such as binder liquids, are substances which are soluble or swellable in water and which solidify at room temperature. This makes it possible to dispense with a subsequent drying step in which, apart from a solvent or the additional water, part of the organic acid would also evaporate.

Particularly suitable protective agents for the agglomeration process and the coating are those which have a softening temperature above 305C, preferably above 605C, in order to avoid deformation of the agglomerates if the storage temperature is relatively high. The protective agents which are preferably used additionally do not counteract the pH-lowering effect of the adsorbed organic acid or even, where appropriate, assist or enhance the latter.

Examples of suitable protective agents are highly concentrated, hot sugar solutions or alkali metal/alkaline earth metal formate/ acetate/propionate solutions. The residual water content thereof can be taken up by the final dusting step. Low-melting polyethylene glycols such as PEG 4000, melts of citric acid, of adipic acid, fumaric acid

BROECKEL et al. Serial No. 09/487,000

or benzoic acid or their salts, highly concentrated solutions of amino acids or mixtures of these acids are suitable and preferred as binder liquids. The amount of binder liquid used is from 0.5 to 80%, preferably 10 to 25%, but particularly preferably 5 to 15%, of the weight of the granules.

Suitable dusting powders are, besides the porous carrier materials themselves, finely disperse, ground organic acids or their salts, eg. sodium formate, and inorganic salts, Sipernats® (highly disperse silica supplied by Degussa), Tixosils® (silica) or Aerosils® (silica supplied by Degussa). The amounts of dusting powders added are 10%, preferably from 0.1 to 5% by weight.

In general, at least one salt of one or more organic acids is introduced into a mixer, eg. an Eirich mixer, and impregnated with at least one organic acid with low energy inputs. However, the process can also be such that the liquid is introduced into the mixer, and the salts of the carboxylic acids are metered in. Higher energy inputs are necessary in the latter case.

Care must be taken to ensure uniform impregnation and to avoid excessive local moistening, which leads to lump formation. After the impregnation, the mixer contains a free-flowing carboxylic acid salt in the form of a crystalline solid. The viscosity of the binder liquid which is subsequently metered in where appropriate should be adjusted,



BROECKEL et al. Serial No. 09/487,000

by appropriate selection of the temperature, so that it is below 1000 mPas, preferably < 100 mPas, in order to achieve a fine drop size distribution in the spraying. In this preferred embodiment, owing to the temperature difference between the hot binder liquid and cooler impregnated salt, the drops of binder liquid initially solidify rapidly. As the agglomeration process progresses, the temperature of the bed increases owing to the mechanical and thermal energy input by from 10 to 305C, depending on the nature of the binder liquid. Further drops of binder liquid become attached to the previously formed agglomerates, and some of them coalesce together. The energy input increases during the agglomeration.

It is possible finally to add an odorizing agent along with the dusting powder as described above. Suitable for this in principle are a large number of fragrances and flavorings which can be selected depending on the subsequent use of the agglomerate. The content of these fragrances can be < 1%, preferably from 0.05 to 0.5%, of the weight of the granules. The agglomerates produced in this way contain little dust and have a reduced odor, and their organic acid content is readily soluble in water.

The novel impregnated salts and/or preservatives are suitable for acid treatment and/or preservation of human and animal foods, for use in silage or for leather treatment.

Human and animal foods mean, in particular, grass, agricultural crops and/or compounded animal food and the materials used to produce them, such as hay, barley,

BROECKEL et al. Serial No. 09/487,000

wheat, oats, rye, corn, rice, soybeans, sugarcane residues, sugarcane, rapeseed, peanuts, sunflower seeds, buckwheat chaff, silage, wet grains, pulse or grain crops, but also milk replacer, liquid, compound and mineral feeds, fish silage or fish, meat or bone meal.

The novel preservatives may also contain other additives such as minerals, vitamins, antibiotics or protein additives. The preservatives may, in particular, contain other additives with fungicidal or bactericidal properties, such as formalin, formic acid, acetic acid, propionic acid, benzoic acid, sorbic acid or bisulfites.

The novel impregnated salts and/or preservatives are advantageously added to the material to be preserved in an amount of, in each case, from 0.1 kg to 25 kg, preferably from 0.5 kg to 20 kg, particularly preferably from 5 to 15 kg, per ton of material to be preserved.

#### Examples

(Purity of the formic acid and propionic acid used = 99%)

#### A. Formic acid

Example 1

100 g of sodium formate were introduced into a household mixer (Braun), and 15% by weight of formic acid were added. The temperature rose from 225C to 405C on uptake of the acid. The resulting product (= impregnated salt) was free-flowing and odorless.

Example 2

100 g of calcium formate were introduced into a household mixer, and 15% by weight of formic acid were added. The resulting product had a slightly pungent odor of formic acid and showed cohesive behavior, ie. the resulting impregnated salt was slightly damp and not free-flowing.

Example 3

100 g of potassium formate were introduced into a household mixer, and 10% by weight of formic acid were added. The temperature rose from 235C to 455C on uptake of the acid. The impregnated salt had a slightly pungent odor and showed a slight tendency to become granular.

B. Propionic acid

Example 4

100 g of fumaric acid were introduced into a household mixer, and 15% by weight of propionic acid were added. The product was highly cohesive and had an intense odor.

Example 5

100 g of sodium formate were introduced into a household mixer, and 15% by weight of propionic acid were added as in the previous examples. The product is highly cohesive and has an intense odor.

Example 6

100 g of calcium formate were introduced into a household mixer, and 15% by weight of propionic acid were added. The temperature rose slightly while the acid was taken up. The product had an intense odor and showed a cohesive behavior.

BROECKEL et al. Serial No. 09/487,000

Example 7

100 g of calcium propionate were introduced into a household mixer, and 15% by weight of propionic acid were added. The temperature rose from 235C to 295C on uptake of the acid. The product is free-flowing and has an intense odor.

C. Production of preservatives

Example 8

1000 g of sodium formate were introduced into an Eirich mixer (RO2) and impregnated with 15% by weight of formic acid. 200 g of sodium formate melt at 805C are sprayed as binder from a heated storage container through a two-component nozzle onto 1000 g of this mixture into the mixing chamber. The resulting agglomerates are dusted with 44 g of Sipernat® (= highly disperse silica supplied by Degussa). The resulting product is free-flowing and odorless.

Example 9

1000 g of sodium formate were introduced into an Eirich mixer and impregnated with 15% by weight of formic acid. For agglomeration and coating, 180 g of a concentrated

BROECKEL et al. Serial No. 09/487,000

glucose solution at 805C are sprayed as binder from a heated storage container through a two-component nozzle into the mixing chamber. The resulting agglomerates are dusted with 45 g of Sipernat<sup>®</sup> (= highly disperse silica supplied by Degussa) and 12 g of citral. The acid content is then 59.5%. The resulting agglomerates are free-flowing.

#### Example 10

As in Example 9, 500 g of sodium formate were introduced into an Eirich mixer and impregnated with 15% by weight of formic acid. Then 500 g of perlite were added. 260 g of citric acid melt at 1705C are sprayed in as binder from a heated storage container through a two-component nozzle into the mixing chamber. The resulting agglomerates are dusted with 44 g of Sipernat<sup>®</sup> (= highly disperse silica supplied by Degussa) and 8 g of vanillin. The total acid content is 29.7%. The resulting preservatives are free-flowing and odorless. The impregnated salts described in Examples 1 to 7 can also be converted as in Examples 8 to 10 into free-flowing preservatives with a reduced odor or no odor.

The following Examples 11 to 14 show storage stability tests for an impregnated salt (sodium formate impregnated with 20% by weight formic acid) treated with various protective agents and/or dusting powders (see Table 1). Part-quantities of the

BROECKEL et al. Serial No. 09/487,000

impregnated salts were placed in a tumbler mixer and mixed for a further 10 min while adding the additives (see Table 1). The products were then introduced into a steel vessel (diameter about 40 mm) up to 15 - 20 mm below the rim of the vessel and stored in a drying oven at 355C under load (simulated with a metal piston), the load corresponding to simulated storage under normal storage conditions, and tested at the stated times. Because of the small diameter of the test vessel and the storage under pressure, in order to establish whether a product is free-flowing or not, it is necessary to tap the vessel. The terms used to indicate the result of the flow test have the following meanings:

gentle tapping 1x, gentle tapping 2x and tapping 1x = product is free-flowing

tapping 3x = product shows caking but is essentially free-flowing

tapping 4x, tapping 5x and tapping >5x = product is caked and essentially no longer free flowing.

Table 1: Storage stability of the impregnated salts

<u>[Exam-ple]</u> <u>Example</u>	<u>Storage</u> <u>time in days</u>	<u>Additive</u>	<u>Flow test</u>	<u>Remarks</u>
<u>11</u>	<u>7 d</u>	<u>1% FK500LS<sup>1</sup></u>	<u>tapping 1x</u>	<u>slightly caked, loose</u>
		<u>2% FK500LS</u>	<u>tapping 1x</u>	<u>no caking</u>
		<u>4% FK500LS</u>	<u>gentle tapping</u> <u>1x</u>	<u>no caking</u>
		<u>1% [Sip.]</u> <u>Sipernat<sup>®</sup>50S<sup>2</sup></u>	<u>gentle tapping</u> <u>2x</u>	<u>caked</u>
		<u>2% [Sip.]</u> <u>Sipernat<sup>®</sup>50S</u>	<u>gentle tapping</u> <u>1x</u>	<u>no caking, dust</u>
		<u>4% [Sip.]</u> <u>Sipernat<sup>®</sup>50S</u>	<u>gentle tapping</u> <u>1x</u>	<u>no caking, dust</u>
<u>12</u>	<u>14 d</u>	<u>1% Aerosil<sup>®</sup> 200<sup>3</sup></u>	<u>tapping 3x</u>	<u>caked</u>
		<u>2% Aerosil<sup>®</sup> 200</u>	<u>tapping 2x</u>	<u>slightly caked</u>



<u>[Exam-ple]</u> <u>Example</u>	<u>Storage</u> <u>time in days</u>	<u>Additive</u>	<u>Flow test</u>	<u>Remarks</u>
		<u>3% Aerosil<sup>®</sup> 200</u>	<u>tapping 1x</u>	<u>no caking</u>
		<u>4% Aerosil<sup>®</sup> 200</u>	<u>=</u>	
		<u>5% Aerosil<sup>®</sup> 200</u>	<u>tapping 2x</u>	<u>no caking, dust</u>
		<u>2% Aerosil<sup>®</sup> 200</u> <u>+ 2% D17<sup>4</sup></u>	<u>tapping 2x</u>	<u>no caking, much dust</u>
		<u>2% D17</u>	<u>tapping 1x</u>	<u>slight caking, dust</u>
		<u>5% D17</u>	<u>tapping 1x</u>	<u>no caking, dust</u>
<u>13</u>	<u>7 d</u>	<u>2% R972<sup>5</sup> + 2%</u> <u>benzoic acid</u>	<u>tapping &gt;5x</u>	<u>very caked</u>
		<u>2% R972 + 2%</u> <u>Na benzoate</u>	<u>tapping &gt;5x</u>	<u>very caked</u>
		<u>2% R972 + 2% K</u> <u>sorbate</u>	<u>tapping &gt;5x</u>	<u>very caked</u>

<u>[Exam-ple]</u> <u>Example</u>	<u>Storage</u> time in days	<u>Additive</u>	<u>Flow test</u>	<u>Remarks</u>
		<u>4% R972</u>	<u>tapping 4x</u>	<u>caked</u>
		<u>2% R972 + 1%</u> <u>FK500LS</u>	<u>tapping 1x</u>	<u>no lumps</u>
		<u>2% R972 + 2%</u> <u>FK500LS</u>	<u>tapping 1x</u>	<u>dust, no lumps</u>
		<u>2% R972 + 2%</u> <u>Zeolite<sup>6</sup></u>	<u>tapping 5x</u>	<u>very caked</u>
		<u>2% R972 + 2%</u> <u>sorbitol</u>	<u>tapping &gt;5x</u>	<u>very caked</u>
<u>14</u>	<u>7</u>	<u>1% Aerosil<sup>®</sup> 200</u>	<u>tapping 3x</u>	<u>caked</u>
		<u>2% Aerosil<sup>®</sup> 200</u>	<u>tapping 2x</u>	<u>slightly caked</u>
		<u>3% Aerosil<sup>®</sup> 200</u>	<u>tapping 1x</u>	<u>slightly caked</u>
		<u>4% Aerosil<sup>®</sup> 200</u>	<u>tapping 3x</u>	<u>not caked, dust</u>

<u>[Exam-ple]</u> <u>Example</u>	<u>Storage</u> time in days	<u>Additive</u>	<u>Flow test</u>	<u>Remarks</u>
		<u>5% Aerosil<sup>®</sup> 200</u>	<u>tapping 3x</u>	<u>not caked, dust</u>
		<u>2% cornmeal</u>	<u>tapping &gt;5x</u>	<u>very caked</u>
		<u>5% cornmeal</u>	<u>tapping &gt;5x</u>	<u>very caked</u>
		<u>2% D17</u>	<u>tapping 1x</u>	<u>slightly caked</u>
		<u>2% D17</u>	<u>tapping 1x</u>	<u>not caked, dust</u>
		<u>1% Aerosil<sup>®</sup> 200</u> <u>+ 2% R972</u>	<u>tapping 1x</u>	<u>not caked</u>
		<u>2% Aerosil<sup>®</sup> 200</u> <u>+ 2% R972</u>	<u>tapping 1x</u>	<u>slightly caked, dust</u>

<sup>1 2 3 4 5</sup> various silicas supplied by Degussa

<sup>6</sup> Zeolite supplied by Degussa

BROECKEL et al. Serial No. 09/487,000

D. Acidification of foodstuffs

Example 15

A piglet starter feed was treated with 10 kg/t or 20 kg/t of an impregnated salt (sodium formate/15% by weight formic acid). The pH of the feed fell from 6.4 to respectively 5.5 or 5.1.

BROECKEL et al. Serial No. 09/487,000

Impregnated salts, their production and their use

Abstract

The present invention relates to impregnated salts comprising at least one salt of one or more carboxylic acids, which salt has been impregnated with from 0.5 to 30% by weight, based on the carboxylic acid salt, of at least one carboxylic acid, and to preservatives comprising an impregnated salt and, where appropriate, at least one carrier and/or formulation auxiliaries, it being possible for the preservatives to be coated with a protective agent and/or a dusting powder.

The invention furthermore relates to a process for producing the impregnated salts and the preservatives, and to the use of the salts and preservatives for the treatment of human and animal food, and for use in silage or for leather treatment.

**VERSION WITH MARKINGS TO SHOW CHANGES MADE IN THE CLAIMS**

Please amend claims 7,10 and 16 as follows.

7. (amended)A preservative as claimed in claim 6, additionally comprising a carrier  
[and/or formulation auxiliaries].

10. (amended)A preservative as claimed in claim 6, further comprising a protective agent selected from the group consisting of [wherein] polyethylene glycols, polyvinylpyrrolidones, [or] C<sub>3</sub>-C<sub>14</sub>[, preferably C<sub>3</sub>-C<sub>6</sub>,] organic acids and their salts, [in particular citric acid, fumaric acid, succinic acid, adipic acid, benzoic acid, sorbic acid and their salts,] and [or] amino acids and their salts[, are used as protective agents].

16. (amended)A process for preserving human and animal food or silage,  
wherein [The use of] the impregnated salts as claimed in claim 1, or [of] the preservatives are added to the human or animal food or silage [for acid treatment, for preserving human and animal food, or for use in silage or for leather treatment].

Add new claims 17-21

17.(newly added) A preservative as claimed in claim 6, additionally comprising formulation auxiliaries.

BROECKEL et al. Serial No. 09/487,000

18.(newly added) A preservative as claimed in claim 10, wherein the protective agent is selected from the group consisting of C<sub>3</sub>-C<sub>6</sub> organic acids and their salts.

19.(newly added) A preservative as claimed in claim 18, wherein the protective agent is selected from the group consisting of citric acid, fumaric acid, succinic acid, adipic acid, benzoic acid, sorbic acid and their salts.

20.(newly added) A process for treating leather wherein leather is contacted with the impregnated salts of claim 1 or the preservatives.

21.(newly added) A process for acid treatment wherein the impregnated salts of claim 1 or the preservatives are introduced into or placed on an item to be treated.

**COPY OF ALL CLAIMS**

1. Impregnated salts comprising at least one salt of one or more carboxylic acids, which salt has been impregnated with from 0.5 to 30% by weight, based on the carboxylic acid salt, of at least one liquid carboxylic acid.
2. Impregnated salts as claimed in claim 1, comprising at least one salt of a C<sub>1</sub>-C<sub>8</sub>-mono- or dicarboxylic acid, which salt has been impregnated with at least one C<sub>1</sub>-C<sub>8</sub>-mono- or dicarboxylic acid.
3. Impregnated salts as claimed in claim 1, comprising at least one salt of a carboxylic acid selected from the group of formic acid, acetic acid or propionic acid, which salt has been impregnated with at least one carboxylic acid selected from the group of formic acid, acetic acid or propionic acid.
4. Impregnated salts as claimed in claim 1, where the carboxylic acids in the carboxylic acid salts and the carboxylic acid used for impregnating the salts are identical.
5. Impregnated salts as claimed in claim 1, wherein the impregnated salts comprise at least one salt of one or more carboxylic acids selected from the group of ammonium, potassium, sodium, lithium, magnesium or calcium salts.

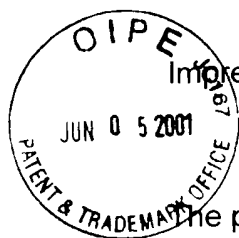


6. A preservative comprising an impregnated salt as claimed in claim 1.
7. A preservative as claimed in claim 6, additionally comprising a carrier.
8. A preservative as claimed in claim 6, which is coated with a protective agent which is soluble or swellable in water at 20° C.
9. A preservative as claimed in claim 6, wherein water-soluble polymers, organic acids, their salts or low-melting inorganic salts are used as protective agents.
10. A preservative as claimed in claim 6, further comprising a protective agent selected from the group consisting of polyethylene glycols, polyvinylpyrrolidones, C<sub>3</sub>-C<sub>14</sub> organic acids and their salts, and amino acids and their salts.
11. A preservative as claimed in claim 6, wherein a dusting powder is applied to the surface in addition to or in place of the protective agent.
12. A process for producing impregnated salts as claimed in claim 1, which comprises impregnating at least one salt of a carboxylic acid or of a mixture of carboxylic acids with at least one liquid carboxylic acid until the concentration is 30% by weight based on the carboxylic acid salt.

13. A process as claimed in claim 12, wherein at least one carboxylic acid is introduced into a mixer, and at least one salt of a carboxylic acid or of a mixture of carboxylic acids is metered in.
14. A process for producing a preservative as claimed in claim 6, which comprises mixing impregnated salts with one or more carriers and/or formulation auxiliaries, and agglomerating with or without the addition of at least one binder.
15. A process as claimed in claim 14, wherein the preservative is coated with a protective agent which is soluble or swellable in water at 20°C and/or if required the flow characteristics of the preservative are ensured by dusting with a finely dispersed dusting powder.
16. A process for preserving human and animal food or silage, wherein the impregnated salts as claimed in claim 1, or the preservatives are added to the human or animal food or silage.
17. A preservative as claimed in claim 6, additionally comprising formulation auxiliaries.
18. A preservative as claimed in claim 10, wherein the protective agent is selected from the group consisting of C<sub>3</sub>-C<sub>6</sub> organic acids and their salts.

BROECKEL et al. Serial No. 09/487,000

18. A preservative as claimed in claim 10, wherein the protective agent is selected from the group consisting of  $C_3$ - $C_6$  organic acids and their salts.
19. A preservative as claimed in claim 18, wherein the protective agent is selected from the group consisting of citric acid, fumaric acid, succinic acid, adipic acid, benzoic acid, sorbic acid and their salts.
20. A process for treating leather wherein leather is contacted with the impregnated salts of claim 1 or the preservatives.
21. A process for acid treatment wherein the impregnated salts of claim 1 or the preservatives are introduced into or placed on an item to be treated.



Impregnated salts, their production and their use

The present invention relates to impregnated salts comprising at least one salt of one or more carboxylic acids, which salt has been impregnated with from 0.5 to 30% by weight, based on the carboxylic acid salt, of at least one carboxylic acid, and to preservatives comprising an impregnated salt and, where appropriate, at least one carrier and/or formulation auxiliaries, it being possible for the preservatives to be coated with a protective agent and/or a dusting powder.

The invention furthermore relates to a process for producing the impregnated salts and the preservatives, and to the use of the salts and preservatives for the treatment of human and animal food, and for use in silage.

Short-chain organic acids such as formic acid, acetic acid or propionic acid are used for acidifying and preserving human and animal food. Disadvantages of these acids are, for example, their liquid state of aggregation at room temperature, the sharp or pungent odor resulting from the low vapor pressure, and their corrosiveness.

In addition, the liquid organic acids can be incorporated in concentrated form, for example into animal food, only with considerable technical complexity.

DE 28 33 727 A1 discloses a particulate fungicidal material which comprises propionic acid and a carrier material. It is said that with this material there is no increase in the

number of mold colonies on stored agricultural harvest products even after incubation for several days. However, it has emerged that material of this type is itself not stable on storage (loss of acid), and the maximum amount of propionic acid which can be applied depends greatly on the carrier material used. In addition, unpleasant odors arise with this material owing to evaporation of the propionic acid.

EP-A-0 590 856 and EP-A-0 608 975 disclose mixtures of solid carboxylic acid salts and solid carboxylic acids with a lower pKa than the carboxylic acid in the salts used. When this mixture is dissolved in water, the carboxylic acids are liberated from the salts by the carboxylic acid with the lower pKa in a displacement reaction. The resulting new salts with the carboxylic acid with the lower pKa are advantageously insoluble in water and precipitate from the solution. A disadvantage of these mixtures is that it is still necessary to use various carboxylic acids with different pKa values for producing the preservatives. In order to ensure that the carboxylic acids are completely liberated from the initial carboxylic acid salts (for example from calcium propionate) on dissolving in water, the carboxylic acids with the lower pKa (for example maleic acid) must be added in at least equimolar amounts based on the carboxyl groups present in the acids. This limits the individual carboxylic acid active substance content. If insoluble carboxylic acid salts are formed in this liberation, they must additionally be removed in a subsequent reaction.

It is an object of the present invention to provide novel compositions for treating human and animal food which do not have the abovementioned disadvantages and can easily

be mixed by the user without difficulty into the human and animal food to be treated. The main aim was to produce a solid composition which has a maximum active substance content and displays very little odor, if any. The solid final product should have good storage, flow and processing properties.

We have found that this object is achieved by the novel impregnated salts comprising at least one salt of one or more carboxylic acids, which salt has been impregnated with from 0.5 to 30% by weight, based on the carboxylic acid salt, of at least one liquid carboxylic acid.

The invention additionally relates to preservatives comprising an impregnated salt of the abovementioned composition. In addition, the preservatives may advantageously comprise at least one carrier and/or formulation auxiliary and, where appropriate, be coated with a protective agent and/or dusting powder.

The invention furthermore relates to a process for producing the impregnated salts, which comprises impregnating at least one salt of a carboxylic acid or of a mixture of carboxylic acids with at least one liquid carboxylic acid until the concentration is 30% by weight based on the carboxylic acid salt.

The invention additionally relates to the production of preservatives comprising an impregnated salt of the abovementioned composition, which comprises impregnated salts comprising at least one salt of one or more carboxylic acids, which salt has been

impregnated with from 0.5 to 30% by weight of at least one liquid carboxylic acid being mixed where appropriate with at least one carrier and/or at least one formulation auxiliary, and being agglomerated with or without addition of one or more binders, and subsequently the preservatives advantageously being provided with a protective agent which solidifies at room temperature (23°C), the protective agent being added in an amount such that the resulting preservatives are coated and, where appropriate, further odorization is effected by, for example, adding fragrances. The preservatives produced in this way may advantageously also be coated with a finely dispersed dusting powder to improve the flow properties of the preservatives.

The novel impregnated salts or preservatives have the advantage that the highly pungent odor of the acid is reduced. The impregnated salts advantageously comprise an active substance content of from 68 to 75% by weight, preferably 70 to 73% by weight, particularly preferably 70 to 72% by weight, as total based on the total amount of carboxylic acids present in the salt and added. Both the novel impregnated salts and the preservatives release the acid content efficiently and rapidly from the solid and have good storage, flow and processing properties.

Liquid organic acids suitable for impregnating the carboxylic acid salts are acids or mixtures of acids which are liquid or become liquid at the processing temperatures, preferably down to <sup>40°C</sup>~~40°C~~ or below.

C<sub>1</sub>-C<sub>8</sub>-mono- and/or dicarboxylic acids and the salts of these C<sub>1</sub>-C<sub>8</sub>-mono- and/or

dicarboxylic acids are advantageously used to produce the impregnated salts or to produce the preservatives. Alkali metal, alkaline earth metal or ammonium salts are suitable. Acids such as formic, acetic and/or propionic acid and their ammonium, calcium, lithium, sodium, magnesium and/or potassium salts are preferably used. The calcium, sodium or ammonium salts are advantageously used. However, also suitable in principle are other acids such as amino acids, hydroxy carboxylic acids, oxo acids or mineral acids such as HCl or  $H_2SO_4$  and their salts, with mineral acids being less preferred. It is possible to use single salts or mixtures of different salts of one carboxylic acid or several carboxylic acids which have been impregnated with one or more acids to produce the impregnated salts. The impregnated salts advantageously consist of the salts of a carboxylic acid which have been impregnated with the same carboxylic acid. The impregnated salts preferably consist of the salt of a carboxylic acid which has been impregnated with the same carboxylic acid. Salts of formic acid and/or propionic acid which have been impregnated with formic acid and/or propionic acid in a form which is as concentrated as possible, for example with 99% strength formic acid, are particularly preferred. Impregnated salts produced from formic acid and the salts of formic acid are very particularly preferred.

X-Ray structural analysis of the novel impregnated salts shows an additional band by comparison with normal carboxylic acid salts.

The impregnated salts can, to improve handling, advantageously be mixed with other substances, for example with a carrier, and/or be dusted with a dusting powder.



5 153  
The term impregnation means applying at least one carboxylic acid, which is liquid at <sup>40°C</sup> 40°C or below, to the solid carboxylic acid salt(s) so that the liquid carboxylic acid(s) penetrate(s) into the salt crystal(s). As a rule, this takes place with slight evolution of heat. For the impregnation, at least one carboxylic acid is applied in an amount of up to 30% by weight, based on the carboxylic acid salt(s), onto the salt(s), preferably applying the carboxylic acid(s) in an amount of from 0.5 to 30% by weight, particularly preferably applying from 15 to 25% by weight, very particularly preferably applying from 15 to 20% by weight, based on the salt component, to produce a solid substance as reaction product. With more than 30% by weight of acid, the salt crystals start to stick together; under these conditions, free carboxylic acid is present to some extent in addition to the impregnated salts. These crystals which are stuck together can be separated from one another by adding a release agent, and the free carboxylic acid can be taken up by the release agent. With more than 35% by weight of acid, the products stick together so strongly that a pasty texture results as a consequence of the free carboxylic acid. These pasty textures can be processed to granules for example in another working step by addition of a release agent and treatment in, for example, a mixer. Since further working steps and larger amounts of a release agent are necessary if more than 30% by weight of free acid is added, these embodiments are less preferred for economic reasons. However, it is possible in principle to improve the flow properties of the impregnated salts by adding small amounts of a release agent even with less than 30% by weight of carboxylic acid. Examples of suitable and advantageous release agents are Sipernats® (highly disperse silica supplied by Degussa), Aerosils® (silica supplied by Degussa) and/or Tixosils® (silica).

Thus, in the novel process for producing the impregnated salts, at least one salt of a carboxylic acid or of a mixture of carboxylic acids is impregnated with at least one carboxylic acid which is liquid at 405C or below until the concentration is 30% by weight based on the carboxylic acid salt(s).

It is also possible in the novel process for producing the impregnated salts to add at least one salt of one or more carboxylic acids to at least one carboxylic acid. This mode of production is less favorable than addition to the salt(s) so that under these conditions, for example when a mixer is used for production, an increased energy input is necessary.

The novel process for producing impregnated salts is advantageously carried out at a temperature determined by the solidification point of the carboxylic acid used. The process is carried out at from 0 to 605C, preferably from 15 to 505C, particularly preferably from 20 to 405C.

In a preferred embodiment, the novel salt also has a protective agent and/or dusting powder on the surface of the crystals. The size of the impregnated salt crystals is preferably below 2.5 mm, particularly preferably from 10  $\mu\text{m}$  to 2000  $\mu\text{m}$ , very particularly preferably from 300  $\mu\text{m}$  to 1500  $\mu\text{m}$ .

The novel preservatives mean preservatives comprising impregnated salts which comprise at least one salt of one or more carboxylic acids and have been impregnated

with at least one liquid carboxylic acid. These impregnated salts can be mixed in the preservatives with one or more carriers and/or formulation auxiliaries. It is possible in the novel process for producing the preservatives to agglomerate this mixture with or without addition of binder. It is then possible to apply to these preservatives a protective agent which is soluble or swellable in water at 205C and/or a finely dispersed dusting powder so that the novel preservatives have a coating of a protective agent and/or dusting powder.

Carriers which can be employed are porous, organic or inorganic carrier materials whose particle sizes are from 1  $\mu\text{m}$  to 1,000  $\mu\text{m}$ , preferably from 5  $\mu\text{m}$  to 100  $\mu\text{m}$ .

Suitable in principle for producing such free-flowing, reduced odor agglomerates are all known organic or inorganic porous carriers as long as they are resistant to acid. Examples are cereal brans, perlite, clay materials, silicates and silicas, with inorganic carriers being preferred because their properties can be controlled better.

Examples of other carriers which can be used are diatomaceous earth, crushed sand, clay, nylon powder, insoluble metal oxides or insoluble metal salts, Aerosil® (silica supplied by Degussa), corundum, ground glass, granite, quartz or flint, aluminum phosphate, kaolin, bentonite, zeolites, calcium silicate, talc, titanium oxide, active carbon or bonemeal.

Carriers which are preferably used are cereal brans, silicates, perlite or silicas in

amounts of from 10% to 70%, preferably 20 to 40%, of the weight of the impregnated salt.

Suitable binders in the novel process are water and/or synthetic or natural polymers, for example albumin, casein, soybean protein, starch, synthetic cellulose derivatives such as carboxymethylcellulose, methylcellulose, hydroxymethyl-, hydroxyethyl- and/or -propylcellulose, polyethylene glycol, polyvinyl alcohol, polyvinylpyrrolidone, gelatin, carrageenan, chitosan, dextrin, alginates, agar-agar, gum arabic, tragacanth or guar gum, or mixtures thereof.

Protective agents which can be used are water-soluble polymers such as synthetic or natural polymers, for example gelatin, carrageenan, alginates or polyvinyl pyrrolidone, organic acids, their salts or low-melting inorganic salts.

Protective agents which are preferably used are polyethylene glycols, polyvinylpyrrolidones or  $C_3$ - $C_{14}$ , preferably  $C_3$ - $C_6$ , organic acids and their salts, in particular citric acid, fumaric acid, succinic acid, adipic acid, benzoic acid and their salts, or amino acids and their salts.

In a preferred embodiment of the novel process for producing the preservatives, the carboxylic acid salt is introduced into a mixer, impregnated with the organic acid, a carrier is admixed where appropriate, and subsequently agglomeration and coating with the protective agent are carried out in the presence or absence of a binder.

The impregnated salts and/or carrier particles are mixed with the protective agent, the latter ordinarily consisting of a highly concentrated solution or melt of substances which are soluble or swellable in water and solidify at room temperature (23°C). This protective agent is preferably applied in the heated state to the impregnated salt and/or carrier particles and mixed with the latter. During this, the protective agent solidifies on the surface of the impregnated salts and/or carrier particles. Suitable mixer operating parameters result in agglomeration of different particles to larger granules.

The size of the granules can be adjusted by processing parameters, for example during the mixing or during the fluidized bed granulation, and by the amount and type of binder or else by subsequent screening or grinding. The granules preferably have an average diameter of less than 3 mm, in particular of 0.3 - 1.3 mm. It is possible where appropriate for residual water to be present in the protective agent used for coating and agglomeration. After the agglomeration process or directly after production of the impregnated salts, residual water can be bound by a dusting process with a dry and finely dispersed dusting powder. It is possible by this dusting process also to prevent the agglomerates or impregnated salts sticking together later and, in addition, to apply, for example, the salt of the organic acid used (eg. sodium or calcium formate or propionate) to the agglomerate or the salts. It is furthermore possible where appropriate to add a fragrance or flavoring, eg. vanillin, tea flavor, citral or fructin, which makes it possible to achieve an additional odor-masking effect which, for example, makes the food attractive for animals to consume.

Protective agents which are preferably employed, such as binder liquids, are substances which are soluble or swellable in water and which solidify at room temperature. This makes it possible to dispense with a subsequent drying step in which, apart from a solvent or the additional water, part of the organic acid would also evaporate.

Particularly suitable protective agents for the agglomeration process and the coating are those which have a softening temperature above 305C, preferably above 605C, in order to avoid deformation of the agglomerates if the storage temperature is relatively high. The protective agents which are preferably used additionally do not counteract the pH-lowering effect of the adsorbed organic acid or even, where appropriate, assist or enhance the latter.

Examples of suitable protective agents are highly concentrated, hot sugar solutions or alkali metal/alkaline earth metal formate/ acetate/propionate solutions. The residual water content thereof can be taken up by the final dusting step. Low-melting polyethylene glycols such as PEG 4000, melts of citric acid, of adipic acid, fumaric acid or benzoic acid or their salts, highly concentrated solutions of amino acids or mixtures of these acids are suitable and preferred as binder liquids. The amount of binder liquid used is from 0.5 to 80%, preferably 10 to 25%, but particularly preferably 5 to 15%, of the weight of the granules.

Suitable dusting powders are, besides the porous carrier materials themselves, finely

disperse, ground organic acids or their salts, eg. sodium formate, and inorganic salts, Sipernats® (highly disperse silica supplied by Degussa), Tixosils® (silica) or Aerosils® (silica supplied by Degussa). The amounts of dusting powders added are 10%, preferably from 0.1 to 5% by weight.

In general, at least one salt of one or more organic acids is introduced into a mixer, eg. an Eirich mixer, and impregnated with at least one organic acid with low energy inputs. However, the process can also be such that the liquid is introduced into the mixer, and the salts of the carboxylic acids are metered in. Higher energy inputs are necessary in the latter case.

Care must be taken to ensure uniform impregnation and to avoid excessive local moistening, which leads to lump formation. After the impregnation, the mixer contains a free-flowing carboxylic acid salt in the form of a crystalline solid. The viscosity of the binder liquid which is subsequently metered in where appropriate should be adjusted, by appropriate selection of the temperature, so that it is below 1000 mPas, preferably < 100 mPas, in order to achieve a fine drop size distribution in the spraying. In this preferred embodiment, owing to the temperature difference between the hot binder liquid and cooler impregnated salt, the drops of binder liquid initially solidify rapidly. As the agglomeration process progresses, the temperature of the bed increases owing to the mechanical and thermal energy input by from 10 to 305C, depending on the nature of the binder liquid. Further drops of binder liquid become attached to the previously formed agglomerates, and some of them coalesce together. The energy input increases

during the agglomeration.

It is possible finally to add an odorizing agent along with the dusting powder as described above. Suitable for this in principle are a large number of fragrances and flavorings which can be selected depending on the subsequent use of the agglomerate. The content of these fragrances can be  $< 1\%$ , preferably from 0.05 to 0.5%, of the weight of the granules. The agglomerates produced in this way contain little dust and have a reduced odor, and their organic acid content is readily soluble in water.

18  
8-12-02  
impregnated  
The novel ~~impregnated~~ salts and/or preservatives are suitable for acid treatment and/or preservation of human and animal foods, for use in silage or for leather treatment. Human and animal foods mean, in particular, grass, agricultural crops and/or compounded animal food and the materials used to produce them, such as hay, barley, wheat, oats, rye, corn, rice, soybeans, sugarcane residues, sugarcane, rapeseed, peanuts, sunflower seeds, buckwheat chaff, silage, wet grains, pulse or grain crops, but also milk replacer, liquid, compound and mineral feeds, fish silage or fish, meat or bone meal.

The novel preservatives may also contain other additives such as minerals, vitamins, antibiotics or protein additives. The preservatives may, in particular, contain other additives with fungicidal or bactericidal properties, such as formalin, formic acid, acetic acid, propionic acid, benzoic acid, sorbic acid or bisulfites.



The novel impregnated salts and/or preservatives are advantageously added to the material to be preserved in an amount of, in each case, from 0.1 kg to 25 kg, preferably from 0.5 kg to 20 kg, particularly preferably from 5 to 15 kg, per ton of material to be preserved.

## Examples

(Purity of the formic acid and propionic acid used = 99%)

### A. Formic acid

#### Example 1

100 g of sodium formate were introduced into a household mixer (Braun), and 15% by weight of formic acid were added. The temperature rose from 225C to 405C on uptake of the acid. The resulting product (= impregnated salt) was free-flowing and odorless.

#### Example 2

100 g of calcium formate were introduced into a household mixer, and 15% by weight of formic acid were added. The resulting product had a slightly pungent odor of formic acid and showed cohesive behavior, ie. the resulting

impregnated salt was slightly damp and not free-flowing.

### Example 3

100 g of potassium formate were introduced into a household mixer, and 10% by weight of formic acid were added. The temperature rose from 235C to 455C on uptake of the acid. The impregnated salt had a slightly pungent odor and showed a slight tendency to become granular.

B. Propionic acid

Example 4

100 g of fumaric acid were introduced into a household mixer, and 15% by weight of propionic acid were added. The product was highly cohesive and had an intense odor.

Example 5

100 g of sodium formate were introduced into a household mixer, and 15% by weight of propionic acid were added as in the previous examples. The product is highly cohesive and has an intense odor.

Example 6

100 g of calcium formate were introduced into a household mixer, and 15% by weight of propionic acid were added. The temperature rose slightly while the acid was taken up. The product had an intense odor and showed a cohesive behavior.

Example 7

100 g of calcium propionate were introduced into a household mixer, and 15% by weight of propionic acid were added. The temperature rose from 235C to 295C on uptake of the acid. The product is free-flowing and has an intense odor.

#### C. Production of preservatives

##### Example 8

1000 g of sodium formate were introduced into an Eirich mixer (RO2) and impregnated with 15% by weight of formic acid. 200 g of sodium formate melt at 805C are sprayed as binder from a heated storage container through a two-component nozzle onto 1000 g of this mixture into the mixing chamber. The resulting agglomerates are dusted with 44 g of Sipernat<sup>®</sup> (= highly disperse silica supplied by Degussa). The resulting product is free-flowing and odorless.

##### Example 9

1000 g of sodium formate were introduced into an Eirich mixer and impregnated with 15% by weight of formic acid. For agglomeration and coating, 180 g of a concentrated glucose solution at 805C are sprayed as binder from a heated storage container through a two-component nozzle into

the mixing chamber. The resulting agglomerates are dusted with 45 g of Sipernat<sup>®</sup> (= highly disperse silica supplied by Degussa) and 12 g of citral. The acid content is then 59.5%. The resulting agglomerates are free-flowing.

#### Example 10

As in Example 9, 500 g of sodium formate were introduced into an Eirich mixer and impregnated with 15% by weight of formic acid. Then 500 g of perlite were added. 260 g of citric acid melt at 170°C are sprayed in as binder from a heated storage container through a two-component nozzle into the mixing chamber. The resulting agglomerates are dusted with 44 g of Sipernat<sup>®</sup> (= highly disperse silica supplied by Degussa) and 8 g of vanillin. The total acid content is 29.7%. The resulting preservatives are free-flowing and odorless. The impregnated salts described in Examples 1 to 7 can also be converted as in Examples 8 to 10 into free-flowing preservatives with a reduced odor or no odor.

The following Examples 11 to 14 show storage stability tests for an impregnated salt (sodium formate impregnated with 20% by weight formic acid) treated with various protective agents and/or dusting powders (see Table 1). Part-quantities of the impregnated salts were placed in a tumbler mixer and mixed for a further 10 min while adding the additives (see Table 1). The products were then introduced into a steel vessel (diameter about 40

mm) up to 15 - 20 mm below the rim of the vessel and stored in a drying oven at 355C under load (simulated with a metal piston), the load corresponding to simulated storage under normal storage conditions, and tested at the stated times. Because of the small diameter of the test vessel and the storage under pressure, in order to establish whether a product is free-flowing or not, it is necessary to tap the vessel. The terms used to indicate the result of the flow test have the following meanings:

gentle tapping 1x, gentle tapping 2x and tapping 1x = product is free-flowing

tapping 3x = product shows caking but is essentially free-flowing

tapping 4x, tapping 5x and tapping >5x = product is caked and essentially no longer free flowing.

Table 1: Storage stability of the impregnated salts

[Exam-ple] Example	Storage time in days	Additive	Flow test	Remarks
11	7 d	1% FK500LS <sup>1</sup>	tapping 1x	slightly caked, loose
		2% FK500LS	tapping 1x	no caking
		4% FK500LS	gentle tapping 1x	no caking
		1% [Sip.] <u>Sipernat</u> <sup>®</sup> 50S <sup>2</sup>	gentle tapping 2x	caked
		2% [Sip.] <u>Sipernat</u> <sup>®</sup> 50S	gentle tapping 1x	no caking, dust
		4% [Sip.] <u>Sipernat</u> <sup>®</sup> 50S	gentle tapping 1x	no caking, dust
12	14 d	1% Aerosil <sup>®</sup> 200 <sup>3</sup>	tapping 3x	caked
		2% Aerosil <sup>®</sup> 200	tapping 2x	slightly caked
		3% Aerosil <sup>®</sup> 200	tapping 1x	no caking
		4% Aerosil <sup>®</sup> 200	-	
		5% Aerosil <sup>®</sup> 200	tapping 2x	no caking, dust
		2% Aerosil <sup>®</sup> 200 + 2% D17 <sup>4</sup>	tapping 2x	no caking, much dust

[Exam-ple] Example	Storage time in days	Additive	Flow test	Remarks
		2% D17	tapping 1x	slight caking, dust
		5% D17	tapping 1x	no caking, dust
13	7 d	2% R972 <sup>5</sup> + 2% benzoic acid	tapping >5x	very caked
		2% R972 + 2% Na benzoate	tapping >5x	very caked
		2% R972 + 2% K sorbate	tapping >5x	very caked
		4% R972	tapping 4x	caked
		2% R972 + 1% FK500LS	tapping 1x	no lumps
		2% R972 + 2% FK500LS	tapping 1x	dust, no lumps
		2% R972 + 2% Zeolite <sup>6</sup>	tapping 5x	very caked
		2% R972 + 2% sorbitol	tapping >5x	very caked
14	7	1% Aerosil <sup>®</sup> 200	tapping 3x	caked
		2% Aerosil <sup>®</sup> 200	tapping 2x	slightly caked
		3% Aerosil <sup>®</sup> 200	tapping 1x	slightly caked
		4% Aerosil <sup>®</sup> 200	tapping 3x	not caked, dust
		5% Aerosil <sup>®</sup> 200	tapping 3x	not caked, dust



[Exam-ple] Example	Storage time in days	Additive	Flow test	Remarks
		2% cornmeal	tapping >5x	very caked
		5% cornmeal	tapping >5x	very caked
		2% D17	tapping 1x	slightly caked
		2% D17	tapping 1x	not caked, dust
		1% Aerosil® 200 + 2% R972	tapping 1x	not caked
		2% Aerosil® 200 + 2% R972	tapping 1x	slightly caked, dust

<sup>1 2 3 4 5</sup>  
, , , , , various silicas supplied by Degussa

<sup>6</sup> Zeolite supplied by Degussa

D. Acidification of foodstuffs

Example 15

A piglet starter feed was treated with 10 kg/t or 20 kg/t of an impregnated salt (sodium formate/15% by weight formic acid). The pH of the feed fell from 6.4 to respectively 5.5 or 5.1.

## Impregnated salts, their production and their use

### Abstract

The present invention relates to impregnated salts comprising at least one salt of one or more carboxylic acids, which salt has been impregnated with from 0.5 to 30% by weight, based on the carboxylic acid salt, of at least one carboxylic acid, and to preservatives comprising an impregnated salt and, where appropriate, at least one carrier and/or formulation auxiliaries, it being possible for the preservatives to be coated with a protective agent and/or a dusting powder, *one to*

*108*  
*1260*

~~The invention furthermore relates to a process for producing the impregnated salts and the preservatives, and to the use of the salts and preservatives for the treatment of human and animal food, and for use in silage or for leather treatment.~~

*1*